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ScienceDirect
Surface & Coatings Technology 201 (2007) 8202–8204
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

X-ray induced reduction of Au and Pt ions on silicon substrates

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Available online 12 March 2007

Abstract

Prolonged exposure to X-rays of $HAuCl_4$, $PtCl_4$ and their mixtures, deposited from an aqueous solution onto a silicon substrate, causes chemical reduction of the metal ions to their metallic states. The corresponding oxidation reaction is the conversion of chloride ions to chlorine. The resultant metal atoms aggregate to form metallic/bimetallic nanoclusters as evidenced from their XPS chemical shifts. Hence, X-rays are usable for in-situ nanoparticle production or for direct-writing applications on silicon substrates.

Keywords: Reduction by X-rays; XPS; Au and Pt nanoclusters; Au–Pt bimetallic nanoclusters

1. Introduction

Preparation of metal nanoparticles is the key step concerning their promising future applications in microelectronics, photonics, catalysis, biochemical-sensors, etc. [1–7]. The conventional routes utilize methods involving deposition of vaporized atoms from the gas phase, or reduction of their salts using electrochemical and/or electroless wet chemical methods. Other unconventional techniques utilizing lasers, ion-beams and X-rays have also been investigated for incorporating metal clusters on to the substrates in the desired chemical and morphological state(s) [8–21]. Use of energetic particle beams and X-rays are particularly attractive since clean lithographic techniques can also be introduced for direct-writing purposes. The feasibility of direct writing using hard X-rays was demonstrated by Ma et al. and a similar process was reported using VUV both generated by synchrotron sources [22,23].

Reduction of metal ions while recording XPS (X-Ray photoelectron spectroscopy) data has been reported and is considered as a nuisance [24–26]. However, a recent study reports on the utilization of X-rays and electron beams for inducing in-situ oligomerization reactions [27,28]. In addition to X-rays, electron, ion, and other energetic particle exposures, which are frequently encountered for cleaning and/or depth-profiling, also cause reduction of certain metal ions to their lower oxidation states [29–34]. The extent of reduction varies drastically from one metal ion to another and extensive efforts had been devoted to correlate this with certain chemical/physical properties of them [24–34]. In one of our earlier work, we had claimed that the extent of X-ray induced reduction could be related with the electrochemical reduction potential of the metal ion [35,36]. Accordingly, gold, having a very high reduction potential of [ϵ^0_{red} (Au^{3+}) = 1.5 V] is one of the most amenable. Information related to the mechanism of the process and/or the fate of the reduced products (especially whether or not cluster formation or nucleation also take place) are needed. From this aspect XPS is particularly suitable since a significant chemical shift develops to correlate with the size of gold clusters [37–46]. Accordingly, we have recently reported an XPS investigation of $HAuCl_4$ deposited on SiO_2/Si substrate and in PMMA matrix where we have demonstrated the formation of gold nanoclusters by X-ray induced reduction [47]. In this contribution we extend our investigation to include $PtCl_4$ and a mixture of the two salts for preparing the more important Au–Pt bimetallic nanoclusters [48–50].

2. Experimental

Si (100) substrate was allowed to stay in concentrated HF solution for 45–60 s to remove native oxide layer and rinsed with deionized water and dried. Afterwards, the substrates were dip-coated by solutions containing ~0.03% (w/v) of (i) tetrachloroauric acid, (ii) tetrachloroplatinate, or (iii) a 50–50 mixture of

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doi:10.1016/j.surfcoat.2006.07.264

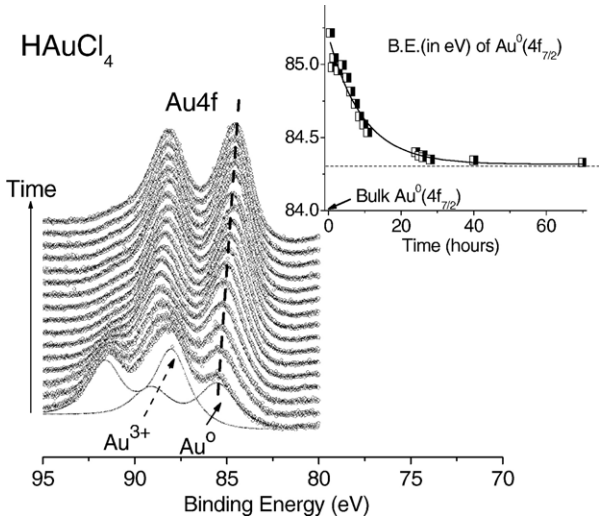

Fig. 1. A set of XPS spectra of the Au4f region of the gold salt deposited on a silicon substrate. The inset shows the variation of the $Au4f_{7/2}$ (Au^0 component).

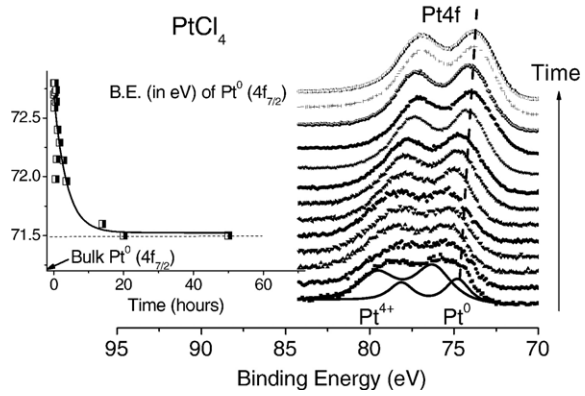

Fig. 2. A set of XPS spectra of the Pt4f region of the platinum salt deposited on a silicon substrate. The inset shows the variation of the $Pt4f_{7/2}$ (Pt^0 component).

them, and dried in air at room temperature. A Kratos ES300 spectrometer with a Mg K_α (not monochromatized) source at 1253.6 eV was used to record the XPS spectra, and at the same time to induce the reduction. The total X-ray power used was 150 W (10 mA, 15 kV), and the base pressure was kept below 10^{-6} Pa throughout the measurements.

3. Results and discussion

In Fig. 1, we display a set of spectra, recorded consecutively while the sample is exposed to X-rays. At the beginning the Au4f peak has a complex shape but can be decomposed into 2 different spin-orbit doublets corresponding to 2 different chemical gold species which can be assigned to Au^{3+} and Au^0 on the basis of their 4f binding energies [35,36]. As time progresses the intensity of the Au^0 doublet increases at the expense of the other doublet, indicating clearly that reduction by X-rays is taking place. The corresponding oxidation process can be followed in the Cl2p region (not shown) which decreases while Au^{3+} is reduced to its metallic state. Intensity of the Cl2p peak decreases and reaches the final atomic ratio of Au:Cl (4:1) as one would expect from the following equation:

$$AuCl_4 + \text{X-rays} \rightarrow Au^0 + 3/2Cl_2(\text{ads.}) + HCl(\text{ads.})$$

The second issue is the shift of the Au^0 peak to lower energies as the time progresses as displayed separately as an inset in Fig. 1. It is well-known that binding energy of gold decreases to that of bulk gold as the particle size of the gold cluster increases and approaches to bulk gold [8,9,37–40]. Our experimental value for the 4f binding energy of Au^0 is 85.3 eV at the beginning and approaches to 84.3 eV. Goodman et al. [39] reported a similar study where binding energy of gold, with different gold coverage, was measured. Although Au^0 particles were prepared by physical vapor deposition method in their study, gold clusters deposited from solution gave similar results to ours. Binding energy of gold cluster changes about 1.8 eV as the gold coverage increases from 0.1 ML to 25 ML. Using the plot depicted by Goodman et. al., average coverage of gold particles obtained from X-ray induced reduction increases from ~0.1 ML to ~4 ML in our study. However, in all the experiments we have carried out, the binding energy of gold particles, deposited from aqueous solution (0.034% (w/v) of $HAuCl_4$) and reduced by X-rays, could not reach the value of the bulk gold (84.00 eV). Hence, as we had already stated in our earlier publication X-rays reduce gold ions and produce stable nanoclusters of gold [47].

A very similar reduction also takes place for Pt^{4+} ions deposited from $PtCl_4$ as shown in Fig. 2, where again reduction and nucleation of the reduced platinum particles can be followed by their XPS spectra. However, as opposed to the case of Au^{3+} ions, complete reduction of Pt^{4+} cannot be realized. More interesting is the bimetallic nanocluster formation when gold and platinum ions are mixed in the solution phase and reduced by X-rays as shown in Fig. 3. Here, we observe that reduction of both metal ions and their nucleation are occurring simultaneously, suggesting the alloy formation as the most likely case. However, further spectroscopic and structural investigations are needed for clarification of this and other related points which are currently underway.

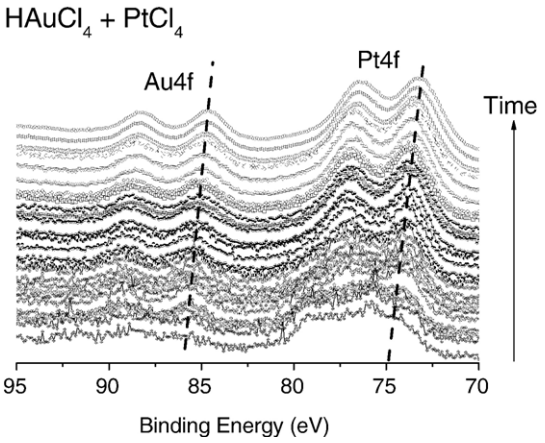

Fig. 3. A set of XPS spectra of the Au4f–Pt4f region of the 50:50 mixture of gold and platinum salts deposited on a silicon substrate. The shifts in the Au4f and Pt4f peaks are highly correlated.

4. Conclusions

X-rays are not chemically innocent and cause reactions. The most important chemical reaction for the Au^{3+} and the Pt^{4+} ions is their reduction to their metallic state, accompanied by oxidation of Cl^- ions to Cl_2. The metal atoms produced quickly aggregate to form metallic nanoclusters as judged by their larger binding energy values compared to their bulk ones. Hence, X-rays, like other energetic particles, can also be used for in-situ preparation of metallic and/or bimetallic nanoparticles, or for direct-writing applications on silicon substrates.

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